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Mercapto 화합물에 의한 은의 정량(제 1 보). 2. 5-Dimercapto-1, 3, 4-Thiadiazol에 의한 은의 전류 적정

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Determination of Silver with Mercaptans (I). Amperometric Titration of Silver with 2. 5-Dimercapto-1, 3, 4-Thiadiazole

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요약 회전백금전극을 지시전극으로하고 수은—요오드화수은(II)을 기준전극으로 하여 암모니아수용액에서 2. 5-dimercapto-1, 3, 4-thiadiazole에 의한 은의 전류적정법을 연구하였다.

암모니아수용액에서 EDTA를 은폐제로 사용하여 여러가지 이온들의 존재하에 미량의 은을 직접 적정할 수가 있었으며 백금과 금 이온만이 방해하였다. 이 방법으로 미량의 은을 상대오차 ±3 % 이내 정량할 수 있다.

Abstract. An amperometric method has been developed for the titration of silver with 2, 5-dimercapto-1, 3, 4, -thiadiazole in ammonical solution (1*N*) using rotating platinum electrode as an indicator electrode and the mercury-mercury (II) iodide as reference electrode. Direct titration of milligram amount of silver (0. 05-1. 0mg) is possible in the presence of a number of foreign ions in ammonical solution containing ethylenediaminetetraacetic acid as masking agent under atmosphere. The interfering elements are gold and platinum. The milligram amount of silver can be determined by the proposed method within an error ±3 %.

Introduction

Numerous amperometric titration methods for the determination of silver have been reported.[1,2,3,4,5] Malinek and Rehak[2] have reported that silver can be titrated with mercapto-phenylthiothiazole and mercapto-benzothiazole in the prosence of ethylenediaminetetraacetic acid (EDTA) as masking agent in a chloride-free medium which contains 0. 01 % gelatin and is adjusted with sodium hydroxide solution so that the pH lies between 5 and 8 (bromocresol purple). Sarena and Sharma[6] recommended the use of pyrovanadate in presence of 20 % alcohol that contains sodium nitrate as the base electrolyte. Bera and Chakrabartty[5] recommemded the use of benzimidazole-2-ylmethanethiol in

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acetate buffer medium (PH 4~5) under nitrogen atmosphere. Berge and Jeroschewsky[7] titrated with thiourea, thionalide, 2-mercaptobenzothiazole and dithio-oxamide. However, none of the methods is satisfactory without separation of the interfering substances.

In an investigation of the properties of the 2, 5, -dimercapto-1, 3, 4-thiadiazole, it was found that 2, 5-dimercapto-1, 3, 4-thiadiazole is precipitated quantitatively with silver in ammonical solution without deaeration.

In the present investigation, a sensitive and specific procedure for the quantitative determination of silver using 2, 5-dimercapto-1, 3, 4-thiadiazole without separation of other cations and anions is developed.

Experimental

Reagents. Analytical reagent grade $HAuCl_4$, $H_2PtCl_66H_2O$, $CuSO_45H_2O$, $HgCl_2$, $Cd(NO_3)4H_2O$, PbO_2, $ZnCl_2$, $NaBiO_3$, EDTA, and distilled water were used throughout.

Standard Solution. Standard silver solution (1 mg/m*l*) was prepared by dissolving 0.4249 g of silver nitrate (Fisher Analytical Reagent A. C. S. Certified) in a 250 m*l* volume-metric flask containing 1 m*l* of concentrated nitric acid and diluting to the mark with water and the strength was confirmed by the Mohr's method. Fresh silver nitrate solution was prepared daily.

Standard solution of 0.01 *M* 2, 5-dimercapto-1, 3, 4-thiadiazole (E. Merk G. R. grade) was prepared by dissolving 0.1502 g of 2, 5-dimercapto-1, 3, 4-thiadiazole in 15 m*l* of concentrated aqueous ammonia solution, diluting to 100 m*l* with water (1 *N* ammonical solution).

Apparatus. A rotating platinum electrode served as the indicator electrode and a mercury-mercury (II) iodide half-cell[8] was used as the reference electrode (potential-0.23 V *v. s.* S. C. E.).

Titration were carried out using a galvanometer with the sensitivity of 0.05×10^{-6} ampere (G-M Laboratories Inc.). A synchronous motor used to rotate the electrode (600 RPM), since the titration completed within a short time.

Titration. Transfer a suitable volume of solution containing 0.05–1.00mg of silver to the titration beaker, add 15 m*l* of 2 *N* ammonia solution and water to make the final volume 30 m*l*.

Titrate the solution with 0.001 *M* 2, 5-dimercapto-1, 3, 4-thiadiazole solution, using rotating platinum electrode and mercury-mercury (II) iodide half-cell short-circurited through a microammeter. The intersection of the two straight line branches of the *L*-shaped titration curve was taken as the end point.

All titrations were carried out under the atmospheric air at room temperature.

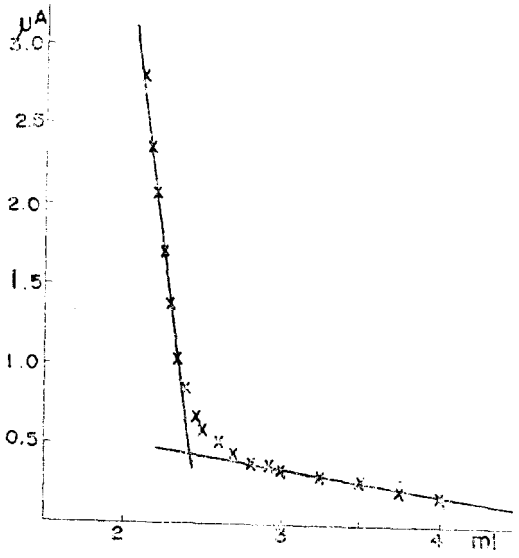

Fig. 1. The amperometric titration curve. 0.50 mg of Ag titrated with 0.001 *M* $C_2H_2N_2S_3$ solution.

Sample Analysis

Procedure. Weigh out about 0.5 g of Ag-alloy (silver ware) and dissolve it in a mixture

Table 1. Effects of pH.

	Ag added, mg	pH	Ag found, mg	dev.	relative error %
*A**	0.050	2—6	0.048	−0.002	4.0
	0.100	2—6	0.099	−0.001	1.0
	0.500	2—6	0.496	−0.004	0.8
	1.000	2—6	0.960	−0.040	4.0
*B**	0.200	9—12	0.201	+0.001	0.5
	0.300	9—12	0.295	−0.005	1.7
	1.000	9—12	1.000	0.000	0.0
*C**	0.050	12	0.050	0.000	0.0
	0.100	12	0.102	+0.002	2.0
	0.500	12	0.496	−0.004	0.8
	1.000	12	1.014	+0.014	1.4

* pH was adjusted with nitric acid in *A*, with ammonia in *B*, and with 1*N* ammonia in *C*, respectivelly.

of 10 m*l* of water and 10 m*l* of nitric acid, boil the solution to expel nitrogen oxides, cool to the room temperature and dilute accurately to 250 m*l*. Transfer to the beaker a suitable aliquot containing 1.0−0.05 mg of silver, neutralize it with ammonia solution and add 15 m*l* of 2 *N* ammonia solution in excess and add 5 m*l* of 0.1 *M* EDTA and water to make the final volume 30 m*l*.

Titrate the silver as mentioned above. The results are shown in *Table* 3.

Results and Discussion

The results are shown in *Table* 1 and 2. The reaction between 2, 5-dimercapto-1, 3, 4-thiadiazole and silver may be due to the formation of a chelate. The addition of an ammonical solution of 2, 5-dimercapto-1, 3, 4-thiadiazole to a solution containing silver ions resulted in a precipitate. One mole of 2. 5-dimercapto-1, 3, 4-thiadiazole was consumed by two moles of silver nitrate in the titration of 0.001 *M* of silver nitrate in 1 *N* ammonical solution with 0.001 *M* of 2, 5-dimercapto-1, 3, 4-thiadiazole under atmospheric air at the room temperature. The precipitate did not show the absorption band of N-H and S-H streching vibration at 3400—3500cm^{-1} and 2550—2600 cm^{-1}, it is considered that the precipitate may have a formula $C_2N_2S_3Ag_2$. The reaction is

$$2\,Ag^+ + RH_2 \longrightarrow RAg_2 + 2H^+$$

From the results shown in the *Table* 1, it can be concluded that reproducible results were obtained in the determination of 0.05—1.00mg of silver when 1 *N* ammonical solution was used.

The silver concentration over the range 10^{-5} to 10^{-7} *M* can be easily followed. Below about 10^{-8} *M* silver concentration the current does not decrease as quickly as it should do, and the results were erratic. From the results shown in the *Table* 2, direct titration were possible in the presence of moderate amounts of Pb, Cd, Zn, Cu, Bi and Hg.

Table 3. Determination of silver in several silver alloys.

Sample	Present method Ag%	Mohr's method Ag%
Chopstick	62.7	62.7
Tea Spoon	72.5	72.5
Spoon	70.1	70.1

Table 2. Determination of silver in presence of foreign ions.

Ag added, mg	Foreign ions present, mg	EDTA added, g	Ag found, mg	dev.	Relative error, %
0.500		0.10	0.496	−0.004	0.8
0.500		0.20	0.483	−0.007	2.1
0.500		1.0	0.495	−0.005	1.0
0.100		1.0	0.100	0.000	0.0
0.100	5.0Hg	1.0	0.102	+0.002	2.0
0.100	10.0Cd	1.0	0.0989	−0.001	1.0
0.100	10.0Bi	1.0	0.0993	−0.001	1.0
0.100	10.0Pb	1.0	0.100	0.000	0.0
0.100	10.0Zn	1.0	0.0993	−0.001	1.0
0.500	1.0Cu	1.0	0.486	−0.014	2.8
0.500	2.0Cu	1.0	0.486	−0.014	2.8
0.500	10.0Cu	1.0	0.507	+0.007	1.4
1.00	30.0Cu	1.0	1.018	+0.018	1.8
0.500	10.0Cu, 10.0Hg	1.0	0.507	+0.007	1.4
0.500	10.0Cd, 10.0Cu, 5.0Hg	1.0	0.486	−0.014	2.8
0.500	20Pb, 20Hg, 10Cd, 10Zn	1.0	0.496	−0.004	0.8
0.100	5.0Hg, 10.0Cd	1.0	0.0971	−0.003	3.0
0.100	5.0Hg, 10.0Cd, 10.0Cu	1.0	0.0982	−0.002	2.0
1.000	10Cu, 10Pb, 10Hg	1.0	1.014	+0.014	1.4
1.000	20Pb, 10Cd, 10Zn, 20Hg	1.0	0.996	−0.004	0.4

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